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EVALUATION OF LONG-CHAIN PHOSPHORUS COMPOUNDS AS LUBRICITY ADDITIVES

Evaluation of Long-Chain Phosphorus Compounds as Lubricity Additives

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Two and 5% blends of a series of new long chain phosphates and phosphonates were examined for suitability as lubricity additives in bis(2-ethylhexyl) sebacate and mineral oil. The most effective anti-wear agents were diethyl stearoxyethyl-, dibutyl lauroxyethyl- and di (2-ethylhexyl) lauroxyethylphosphonate and dibutyl lauroxypropyl phosphate, the most promising extreme pressure agents were di(2-ethylhexyl) lauroxyethyl phosphonate, diethyl oleoxyethyl, diethyl oleoxybutyl, and dibutyl lauroxypropyl phosphates. Coefficient of friction measurements using steel on steel varied from that of the base fluid to 0.04. The latter was obtained with dibutyl lauroxypropyl, diethyl oleoxyethyl, and diethyl oleoxybutyl phosphates.

The lubricity properties of the long chain phosphorus additives compare favorably with the values determined on presently used hypoid gear oils.

The phosphorus derivatives also improved the oxidation stability of the diester but there appeared to be no improvement in rust prevention in either the sebacate or mineral oil.

Introduction

EXTREME pressure and anti-wear additives are used in lubricants industrially to prevent galling, scoring and seizure, and to reduce or minimize wear. Compounds containing elements such as sulfur, chlorine or phosphorus have been used as anti-wear and extreme pressure agents for many years. A survey of the patent literature (1–3) disclosed that phosphorus compounds rank high in their use as lubricity additives. For example, triphenyl, tritolyl, oleyl lauryl phosphates and a mixture of mono and dilauryl phosphates have been used in truck crankcase and gear lubricants, alkyl and aryl esters of phosphoric acid in lubricants for cadmium–silver bearing metals, alkyl and aryl esters of phosphoric acid in sulfurized mineral oils as lubricants for metal fabrications, and esters of phosphoric acid made from oxo alcohols have been used as extreme pressure agents.

Work in recent years at the Eastern Regional Research Laboratory, Department of Agriculture, Phila., Pa., has been directed toward preparation of new phosphorus derivatives of fatty acids of various types (4–6). Consideration of the structures of these new compounds together with the fact that the fatty acid starting materials are abundantly available, made it appear desirable to investigate them for possible use as lubricity additives. Evaluations were conducted at the Research and Development Group, Frankford Arsenal, Philadelphia, Pa. primarily on the dialkyl acyloxyalkyl phosphates (Fig. 1) and dialkyl acyloxyalkyl phosphonates (Fig. 2).

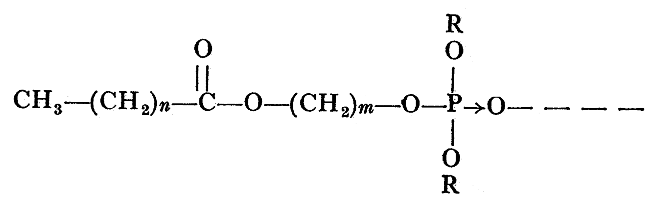

FIG. 1. Dialkyl acyloxyalkyl phosphate: $n = 10$ or 16, $m = 2$ to 4, R = ethyl or butyl.

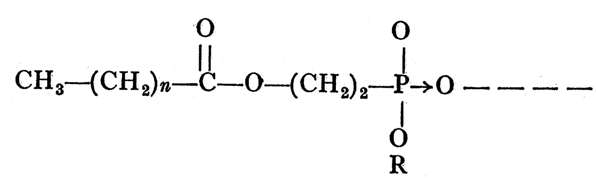

FIG. 2. Dialkyl acyloxyalkyl phosphonate: $n = 10$ or 16, R = ethyl, butyl or 2-ethylhexyl.

The results obtained on the new additives were compared with commercially-available phosphorus additives and currently used hypoid gear mineral oils containing phosphorus, chlorine and sulfur additives.

Experimental

Preparation of Additives

The additives were prepared by reacting trialkyl phosphites with intermediates derived from saturated fatty acids and oleic acid or from dialkyl chlorophosphates and fatty alcohols. The methods of preparation and analytical

Contribution by the ASLE Technical Committee on Properties of Lubricants and presented at the Annual Meeting of the American Society of Lubrication Engineers held in Buffalo, N.Y., April 1959.

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data of the compounds used in this study have been reported elsewhere (4–6) and consequently will not be repeated here. Suffice to say that characterization of the additives included a determination of percentage phosphorus and that the "found" and "calculated" values were in close agreement.

Evaluation of Additives

The additives were evaluated in SAE 40 and 90 mineral oils and in bis(2-ethylhexyl) sebacate. The latter fluid was included since it is typical of the dicarboxylic acid esters currently used as base oils in the formulation of many lubricants used by the military. Two and 5% blends were prepared and subjected to extreme pressure, anti-wear, coefficient of friction, rust prevention and accelerated oxidation studies. These evaluations were conducted with commonly used laboratory bench equipment such as Shell-4-Ball Extreme Pressure and Wear Testers, Falex Extreme Pressure, and a modified Bowden and Leben Coefficient of Friction apparatus. Oxidation stability and rust prevention were determined by techniques previously described (7,8).

Anti-wear properties were determined using the Shell-4-Ball Wear Tester. This instrument operates under the four ball principle first used by Boerlage (9). Approximately 10 ml of the test oil were placed in the test cup so that the three bottom stationary balls were covered to about a 2 ml depth. After positioning the cup on its stand in contact with the fourth ball, the oil was heated to 120 C, 50 kg were placed on the weight tray, and the upper ball was allowed to rotate at 600 rev/min for 1 hr. The diameters of the circular scars worn on the three stationary balls were measured by means of a low-power microscope. The measurements both parallel and normal to the wear scars were averaged and expressed in millimeters of wear scar diameters. The differences in the individual measurements were within five per cent. These data are in Table 1 and show that many of the dialkyl acyloxyalkylphosphonates and phosphates appear to be effective anti-wear additives in both diester and mineral oils.

The value of compound nos. 5, 9, 20 and 22 (Table 1) are approximately of the same low level as tricresyl phosphate which is at present extensively used as an effective anti-wear agent in both synthetic and petroleum oils.

Anti-wear data were also determined on several SAE grade hypoid gear oils presently used in motor vehicles. The data on di(2-ethylhexyl) lauroxyethylphosphonate and dibutyl lauroxypropyl phosphate in SAE 90 mineral oil compare favorably with the values obtained for the commercial products.

Extreme pressure properties were determined with the Shell-4-Ball and the Falex Extreme Pressure Testers.

The Shell-4-Ball Extreme Pressure machine is similar to the Wear Tester except that it is more rigidly built and designed to accommodate higher loads. This instrument was used to determine loads at incipient seizure and at welding. Incipient seizure is defined as the load at which a sudden sizeable increase in wear scar diameter occurs, and welding is the load at which motion of the upper rotating ball in relation to the other three is no longer possible (10). In these tests, wear scar diameters were measured after 1 minute at loads successively increasing in 10 kg increments until incipient seizure, and thereafter in 20 kg increments until welding. A fresh sample of approximately 8 ml and new balls were used at each load. The machine was operated at 600 rev/min.

The Falex Extreme Pressure Tester is a device in which a steel pin is rotated between two Vee shaped steel blocks positioned in the jaws of the load applying mechanism (11). Load is applied by engaging the load applying arm with the ratchet wheel. This action is similar to that of a mechanically operated nut cracker. With the Vee blocks in their recesses, the oil cup was filled to the level mark by the addition of 55 ml of the test fluid. The filled cup was positioned on its holder so that the blocks and pins were covered. The load arms were drawn together and the load gauge assembly was slipped over the load arms. The ratchet wheel was turned by hand until 1000 lb had been applied. This was to make sure that the Vee blocks were set in the proper position. The ratchet wheel was then released and the jaw load gauge and the torque gauge were both set at zero. The eccentric arm of the ratchet wheel was engaged and operated until 250 lb had been applied. The eccentric wheel was then disengaged while the machine remained in operation for 1 min at this load. This procedure was repeated at successively increased loads of 250 lb increments until failure. Excessive squealing or rupture of the pin was considered failure.

The Shell-4-Ball and Falex extreme pressure results are in Table 2. An important application for extreme pressure agents is in the formulation of hypoid gear lubricants. A comparison is made with typical hypoid gear oils currently used which contain phosphorus, chlorine and sulfur additives. It is readily seen that values of the new phosphorus derivatives of the fatty acids in mineral oil, such as phosphonate compound nos. 22, 23 and all the dialkyl acyloxyalkyl phosphate compounds, i.e. nos. 24 to 30 (Table 2) compare favorably with the commercial oils tested. This would seem to indicate that these additives may be useful for hypoid gear applications. The results using the additives in the diester fluid are also worthy of note. A comparison is made with extreme pressure di and trialkyl acid phosphite additives, compound nos. 16, 17 and 18 (Table 2), which are presently used as lubricity agents in diester lubricating oils developed for applications in which high unit pressures are encountered and have been successfully used by the Research and Development Group, Frankford Arsenal, in the formulation of a lubricant to permit operation of revolving type automatic aircraft weapons. The results show many of the new materials have values comparable to the commercial additives, especially compound nos. 5, 11 and 12.

Coefficient of friction measurements were determined with a modified Bowden and Leben apparatus (12). This instrument consists of a flat sliding surface and a stationary upper surface in the form of a steel ball. The flat sliding surface is mounted on a motor-driven carrier. The ball is elastically restrained and is housed in an aluminium ring on which is mounted four strain gauges. These strain gauges are connected in circuit with a Sanborn recorder equipped with two pens. Normal load is applied by placing weights on the top of the aluminium ring; this results in an unbalance which is picked up and measured by the Sanborn recorder. The frictional (tangential) force set up by movement of the lower plate is also measured. Coefficient of friction is calculated as the ratio between tangential and normal force.

The WD-1020 steel plates used in the measurement of coefficients of friction were prepared by polishing with 1/0, 3/0 and 5/0 emery paper, washed in boiling benzene, wiped with clean cotton, washed in boiling petroleum ether and finally flash-dried. A few drops of the test oil were added to the steel plate and allowed to spread over the entire surface. The coated panel was allowed to drain. The 52100 steel balls were cleaned by immersion in petroleum ether and flash-dried. The oil-coated panel then positioned under the steel ball upon which a 100 g load had been placed and the instrument then operated at ambient room temperature at a speed of 0.94 in/min. The coefficient of friction values in Table 3 are the average

TABLE 1

Comparative Anti-wear Data on Additive-containing Oils[a]

Oil	Additive	Shell-4-Ball wear scar diameter[b] (mm)
1	none	0.859
2	diethyl lauroxyethylphosphonate	0.751
3	diethyl lauroxyethylphosphonate (5%)	0.557
4	dibutyl lauroxyethylphosphonate	0.562
5	diethyl stearoxyethylphosphonate	0.510
6	di(2-ethylhexyl) lauroxyethylphosphonate	0.546
7	diethyl lauroxyethyl phosphate	0.729
8	diethyl lauroxypropyl phosphate	0.645
9—Bis(2-ethylhexyl) sebacate	dibutyl lauroxypropyl phosphate	0.501
10	dibutyl lauroxypropyl phosphate (5%)	0.587
11	diethyl oleoxyethyl phosphate	0.773
12	diethyl oleoxybutyl phosphate	0.795
13	diethyl oleoxybutyl phosphate (5%)	0.588
14	trioleyl phosphate	0.586
15	triethyl-α-phosphonolaurate	0.571
16	tricresyl phosphate[c]	0.433
17	tricresyl phosphate (5%)[c]	0.401
18	none	0.734
19	diethyl lauroxyethylphosphonate	0.876
20	dibutyl lauroxyethylphosphonate	0.510
21	diethyl stearoxyethylphosphonate	0.600
22	di(2-ethylhexyl) lauroxyethylphosphonate	0.563
23	diethyl lauroxyethyl phosphate	0.819
24	diethyl lauroxypropyl phosphate	0.797
25	dibutyl lauroxypropyl phosphate	0.675
26—SAE 40 mineral oil	dibutyl lauroxypropyl phosphate (5%)	0.602
27	diethyl oleoxyethyl phosphate	0.609
28	diethyl oleoxybutyl phosphate	0.811
29	diethyl oleoxybutyl phosphate (5%)	0.776
30	trioleyl phosphate	0.923
31	triethyl-α-phosphonolaurate	0.779
32	tricresyl phosphate[c]	0.556
33	tricresyl phosphate (5%)[c]	0.504
34	none	0.637
35	diethyl lauroxyethylphosphonate	0.753
36	di(2-ethylhexyl) lauroxyethylphosphonate	0.528
37—SAE 90 mineral oil	diethyl oleoxybutyl phosphate (5%)	0.785
38	dibutyl lauroxypropyl phosphate (5%)	0.557
39	commercial product[d]	0.525
40 SAE 80 mineral oil	none	0.642
41 SAE 80 mineral oil	commercial product[d]	0.452
42 SAE 140 mineral oil	none	0.564
43 SAE 140 mineral oil	commercial product[d]	0.522
44 SAE 250 mineral oil	none	0.565
45 SAE 250 mineral oil	commercial product[d]	0.422

of five measurements. Variations among the five individual values were within 10%. The coefficient of friction values of the dialkyl acyloxyalkyl phosphates, especially compounds 8, 9 and 10 (Table 3) are noteworthy as is evident comparison with conventional fatty acid and phosphorus type lubricity agents (compound nos. 13 to 18).

Comparison has also been made between coefficient of friction values of the new compounds and phosphorus type lubricity additives in both diester and mineral oil base fluids. These data indicated that diester blends 27, 29 and 31 and mineral oil blends 44 and 48 (Table 3) have coefficient of friction values (0.10) of comparable level to those of effective commercial lubricity additives.

TABLE 2

Comparative Extreme Pressure Data on Additive-containing Oils[a]

Oil	Additive	Extreme seizure load (kg)	Pressure weld load (kg)	Falex extreme pressure jaw load at failure (lbs)
1	none	50	100	1000
2	diethyl lauroxyethylphosphonate	60	180	1500
3	dibutyl lauroxyethylphosphonate	60	180	1750
4	diethyl stearoxyethylphosphonate	60	180	1500
5	di(2-ethylhexyl) lauroxyethylphosphonate	90	180	3250
6	diethyl lauroxyethyl phosphate	110	140	2000
7	diethyl lauroxyethyl phosphate (5%)	80	180	1750
8	diethyl lauroxypropyl phosphate	80	160	1750
9	dibutyl lauroxypropyl phosphate	90	180	1750
10—Bis (2-ethylhexyl) sebacate	dibutyl lauroxypropyl phosphate (5%)	90	160	1750
11	diethyl oleoxyethyl phosphate	110	160	2500
12	diethyl oleoxybutyl phosphate	130	160	2250
13	diethyl oleoxybutyl phosphate (5%)	120	180	2250
14	trioleyl phosphate	70	100	1250
15	triethyl-α-phosphonolaurate	60	100	1250
16	triisopropyl phosphite (5%)[b]	80	140	1750
17	diisopropyl phosphite (1%)[b]	110	160	1750
18	di(2-ethylhexyl) phosphite (1%)[b]	110	160	2250
19	none	50	140	600
20	diethyl lauroxyethylphosphonate	80	180	1250
21	dibutyl lauroxyethylphosphonate	100	180	1250
22	diethyl stearoxyethylphosphonate	70	160	1500
23	di(2-ethylhexyl) lauroxyethylphosphonate	100	180	1750
24	diethyl lauroxyethyl phosphate	70	180	1500
25—SAE 40 mineral oil	diethyl lauroxypropyl phosphate	70	160	1500
26	dibutyl lauroxypropyl phosphate	70	160	2000
27	dibutyl lauroxypropyl phosphate (5%)	120	180	2750
28	diethyl oleoxyethyl phosphate	80	180	1750
29	diethyl oleoxybutyl phosphate	70	140	1500
30	diethyl oleoxybutyl phosphate (5%)	110	180	1500
31 SAE 40 mineral oil	trioleyl phosphate	40	120	750
32 SAE 40 mineral oil	triethyl-α-phosphonolaurate	50	100	500
33	none	40	100	500
34	diethyl lauroxyethylphosphonate	100	180	1000
35	di(2-ethylhexyl) lauroxyethylphosphonate	60	170	750
36	diethyl oleoxybutyl phosphate (5%)	110	180	1500
37—SAE 90 mineral oil	dibutyl lauroxypropyl phosphate (5%)	100	180	1500
38	commercial product[c]	100	180	1750
39	none	50	120	500
40	commercial product[c]	100	200	1500
41 SAE 140 mineral oil	none	40	100	500
42 SAE 140 mineral oil	commercial product[c]	100	140	1500
43 SAE 250 mineral oil	none	40	120	500
44 SAE 250 mineral oil	commercial product[c]	100	220	1500

TABLE 3

Comparative Coefficient of Friction Data on Additive-containing Oils[a]

Oil	Additive	Coefficient of Friction
1	none[b]	0.45
2	diethyl lauroxyethylphosphonate	0.11
3	dibutyl lauroxyethylphosphlonate	0.10
4	diethyl stearoxyethylphosphonate	0.06
5	di(2-ethylhexyl) lauroxyethylphosphonate	0.09
6	diethyl lauroxyethyl phosphate	0.09
7	diethyl lauroxypropyl phosphate	0.08
8	dibutyl lauroxypropyl phosphate	0.04
9—None	diethyl oleoxyethyl phosphate	0.04
10	diethyl oleoxybutyl phosphate	0.04
11	trioleyl phosphate	0.10
12	triethyl-α-phosphonolaurate	0.08
13	lauric acid[c]	0.10
14	oleic acid[c]	0.08
15	stearic acid[c]	0.05
16	tricresyl phosphate[d]	0.07
17	mixed mono and dialkyl acid phosphate[d]	0.06
18	dialkyl acid phosphate[p]	0.07
19	none	0.15
20	diethyl lauroxyethylphosphonate	0.16
21	diethyl lauroxyethylphosphonate (5%)	0.13
22	dibutyl lauroxyethylphosphonate	0.15
23	diethyl stearoxyethylphosphonate	0.11
24	di(2-ethylhexyl) lauroxyethylphosphonate	0.11
25	diethyl lauroxyethyl phosphate	0.15
26	diethyl lauroxypropyl phosphate	0.18
27—Bis (2-ethylhexyl) sebacate	dibutyl lauroxypropyl phosphate	0.10
28	dibutyl lauroxypropyl phosphate (5%)	0.14
29	diethyl oleoxyethyl phosphate	0.09
30	diethyl oleoxybutyl phosphate	0.11
31	diethyl oleoxybutyl phosphate (5%)	0.09
32	trioleyl phosphate	0.14
33	triethyl-α-phosphonolaurate	0.13
34	tricresyl phosphate (5%)	0.10
35	mixed mono and dialkyl acid phosphate[d]	0.08
36	dialkyl acid phosphite[d]	0.10
37	none	0.13
38—SAE 40 mineral oil	diethyl lauroxyethylphosphonate	0.17
39	dibutyl lauroxyethylphosphonate	0.12
40	diethyl stearoxyethylphosphonate	0.12
41	di(2-ethylhexyl) lauroxyethylphosphonate	0.12
42	di(2-ethylhexyl) lauroxyethylphosphonate (5%)	0.12
43	diethyl lauroxyethyl phosphate	0.12
44	diethyl lauroxypropyl phosphate	0.11
45	dibutyl lauroxypropyl phosphate	0.14
46	diethyl oleoxyethyl phosphate	0.12
47—SAE 40 mineral oil	diethyl oleoxybutyl phosphate	0.12
48	diethyl oleoxybutyl phosphate (5%)	0.09
49	trioleyl phosphate	0.12
50	triethyl-α-phosphonolaurate	0.14
51	tricresyl phosphate[d]	0.07
52	mixed mono and dialkyl acid phosphate[d]	0.07
53	dialkyl acid phosphate[d]	0.07
54	none	0.17
55	diethyl lauroxyethylphosphonate	0.12
56—SAE 90 mineral oil	di(2-thylhexyl) lauroxyethylphosphonate	0.12
57	dibutyl lauroxypropyl phosphate (5%)	0.11
58	diethyl oleoxybutyl phosphate (5%)	0.10
59	commercial product[e]	0.10

TABLE 3

Comparative Coefficient of Friction Data on Additive-containing Oils[a]—(contd.)

	Oil	Additive	Coefficient of friction
60	SAE 80 mineral oil	none	0.16
61	SAE 80 mineral oil	commercial product[e]	0.12
62	SAE 140 mineral oil	none	0.16
63	SAE 140 mineral oil	commercial product[e]	0.10
64	SAE 250 mineral oil	none	0.17
65	SAE 250 mineral oil	commercial product[e]	0.10

[a]Unless otherwise indicated blends contain 2% additives.
[b]Bare steel ball sliding on bare steel plate.
[c]Conventional fatty acid lubricity additives.
[d]Commercial phosphorus additives.
[e]Commercial hypoid gear oils containing phosphorus, sulfur and chlorine additives.

Oxidation Inhibiting Properties

The additives were evaluated in bis(2-ethylhexyl)sebacate and mineral oil. Two per cent blends were prepared and subjected to accelerated oxidation tests. Duplicate tests were run on 25 g samples of each blend. Clean, dry air, 5 ± 0.5 l./hr. was bubbled through the oil in the presence of weighed copper and steel catalysts strips immersed in the oil. Tests were run at 100 C for 168 hr, during which time volatile acids were trapped in potassium hydroxide solution. After oxidation, volatile acids as milligrams KOH per gram of oil, and change in weight of the metal strips, change in viscosity at 100 F, and change in neutralization number were determined and used as criteria of stability. These data are in Table 4. They indicate that the new phosphorus

TABLE 4

Comparative Oxidation Data on Additive-containing Oils[a,b]

Oil	Additive	Change in neutralization no.[c]	Volatile acids formed, Eq. mg of KOH	Change in Viscosity (cS) at 100 F	Change in wt. of metal strips (mg) Copper	Steel	Condition of metal strips Copper	Steel
Bis(2-ethylhexyl, sebacate	none	+4.06	2.10	+0.84	+0.81	−0.32	lt. tarn	clean
	diethyl lauroxyethylphosphonate	+0.08	0.33	+0.15	+.17	+0.06	lt. tarn	clean
	di(2-ethylhexyl) lauroxyethyl phosphonate	+0.09	0.46	+0.50	+0.18	+0.10	lt. tarn	clean
	dibutyl lauroxypropyl phosphate	+2.14	0.16	+0.80	+0.16	+0.01	lt. tarn	clean
	diethyl oleoxybutyl phosphate	+0.28	0.22	+0.30	+0.58	+0.02	darkened	clean
	trioleyl phosphate	+9.70	2.62	−0.20	+0.15	+0.06	clean	clean
	triethyl-α-phosphonolaurate	+0.90	0.40	+0.50	+0.02	+0.04	lt. stain	clean
	oxidation inhibitor + diisopropyl phosphite (1%)[d]	+4.93	0.51	+0.10	+0.04	+0.02	lt. stain	clean
	oxidation inhibitor + di(2-ethyl-hexyl) phosphite (1%)[d]	+4.71	0.55	+0.10	+0.52	+0.12	etch stain	clean
	none	+1.04	0.28	+3.10	+0.03	+0.05	tarn stain	clean
	diethyl lauroxyethylphosphonate	+1.45	0.46	+9.60	−0.07	−0.05	lt. stain	clean
SAE 40 mineral oil	di(2-ethylhexyl) lauroxyethyl-phosphonate	+0.98	0.63	+9.00	+0.31	+0.07	etch stain	clean
	dibutyl lauroxypropyl phosphate	+0.54	6.23	+104.2	−0.35	−0.02	etch stain	clean
	diethyl oleoxybutyl phosphate	+5.44	3.15	+23.0	−1.14	−0.07	etch stain	clean
	trioleyl phosphate	+1.06	0.66	+3.90	−0.10	−0.10	etch stain	clean
	triethyl-α-phosphonolaurate	+1.04	0.80	+6.85	+0.03	+0.02	tarn stain	clean
SAE 90 mineral oil	none	+1.12	0.40	+3.60	−0.05	−0.03	stains	clean
SAE 90 mineral oil	commercial product[e]	+0.10	0.27	+13.50	+0.15	−0.03	tarn stain	clean